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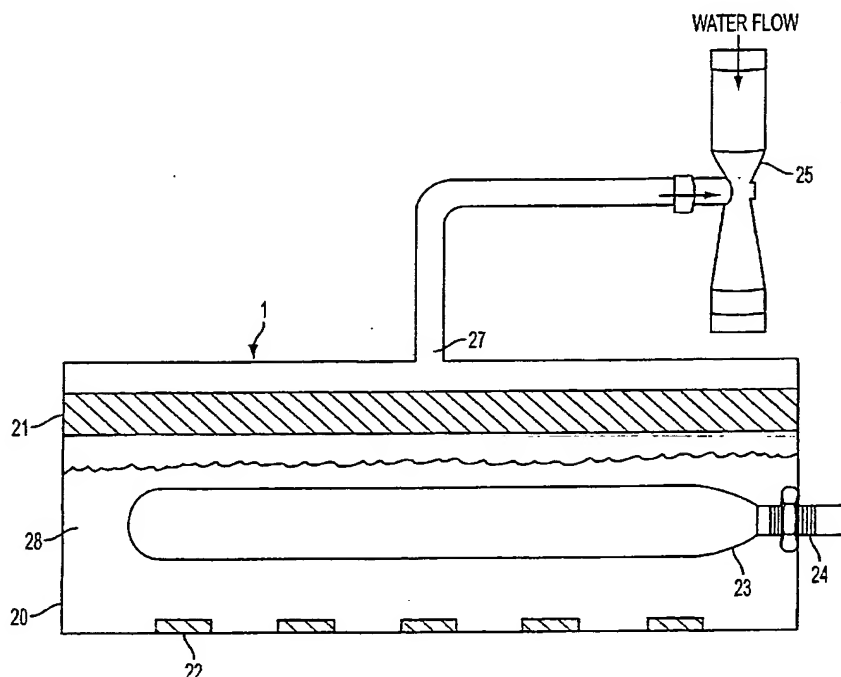
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(54) Title: APPARATUS AND METHOD FOR PRODUCING CHLORINE DIOXIDE



(57) Abstract: Provided is an apparatus (1) and method for making chlorine dioxide on demand by converting a chlorine dioxide generating solution (28) into chlorine dioxide by exposure to UV light (23) in the presence of ultrasonic vibrations (22).

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APPARATUS AND METHOD FOR PRODUCING CHLORINE DIOXIDE

This application claims priority to U.S. Provisional Patent Application Serial No. 60/492,729, filed August 6, 2003, the
5 complete disclosure of which is incorporated herein by reference.

1. Field of the Invention

The present invention relates to an apparatus and method for production of
10 chlorine dioxide from readily available raw materials. More specifically, the invention relates to an apparatus and method for converting a chlorine dioxide generating solution into chlorine dioxide on demand by exposure to UV light.

2. Background of the Invention.

15 Chlorine dioxide enjoys considerable commercial and industrial importance in a wide variety of applications. It is currently used in large quantities as a bleaching agent for wood pulp, paper, fats, oils, tallow, and flour.

20 A recent series of regulatory approvals have increased the use of chlorine dioxide as a disinfectant and sanitizer in the food processing industry. New federal guidelines have permitted its use in meat, dairy, poultry, fruit and vegetable post-harvest produce, and prepared foodstuffs. In most circumstances, chlorine dioxide does not cause organoleptic impairments of food
25 products.

Chlorine dioxide is also widely used in the wastewater industry both as a pollution control agent and a potable water treatment. Chlorine dioxide is an excellent sulfide scavenging agent and is employed in scrubbing towers in wastewater,
30 rendering, and the oil and gas industry.

The unique properties of chlorine dioxide provide a growing receptivity in its use as an environmental and microbial control agent. Chlorine dioxide reacts with a high degree of specificity towards certain industrial pollutants, such as sulfides,
35 amines, mercaptans, and cyanide while not reacting with ammonia or most organic compounds.

The highly selective nature of chlorine dioxide is important in disinfection. Unwanted disinfection by-products such as trihalomethanes (THMs) and polychlorobiphenyls (PCBs) are not formed as they are with chlorine or
5 hypochlorites. Chlorine dioxide also is effective over a wide pH range, does not disassociate in solutions, has rapid disinfection kinetics, and does not accumulate in treated solutions.

Chlorine dioxide is most often generated on-site due to prohibition and hazards
10 of its transport and storage. It has been produced conventionally by several chemical and electrochemical processes. The most common means of production is the acidification of aqueous sodium chlorite. Strong acids such as sulfuric or hydrochloric give high yields of chlorine dioxide while weaker (and safer) acids such as citric and lactic give much lower yields.

15

The acidic conversion of chlorite to chlorine dioxide is greatly enhanced in yield by adding a chlorine donor such as hypochlorite or chlorine gas. While advantageous in recoverable yield, a three-precursor system introduces a greater level of complexity in apparatus and reactor design. Current methods for
20 producing chlorine dioxide gas employ highly toxic chlorine gas. On-site storage of hypochlorites, strong acids, and chlorine gas also poses additional hazards and regulatory scrutiny to the end user.

Electrochemical generators have attempted to partially address this issue. Such
25 generators utilize a single precursor, normally sodium chlorite or sodium chlorate. The produced chlorine dioxide product is separated from the electrolyte solution using a gas permeable structure. However, they are not widely used due to other disadvantages such as high cost, generation of explosive hydrogen gas, and reliability. New designs have begun to address these concerns

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A potentially superior and alternative method for producing chlorine dioxide is by photochemical oxidation. Photochemical reactions of chlorine dioxide and

oxyanions of chlorine have been reported by E.J. Brown and M. Cheung (1932) and disclosed in US Patent Nos. 2,043,284, 2,457,285, and 2,683,651.

5 More recent work of photochemical methods is disclosed in U.S. Patent Nos. 4,414,180 and 4,456,511 to Fisher. This work describes a generator containing aqueous sodium chlorite illuminated by externally placed incandescent fluorescent bulbs. The sodium chlorite is photochemically oxidized to chlorine dioxide and removed from the aqueous solution with a gaseous nitrogen or air stream.

10 Further, more detailed work is disclosed in US Patent No. 4,874,489 to J. Callera, which describes a tubular chamber containing sodium chlorite. An ultraviolet source, namely a low pressure mercury vapor bulb, was housed inside the vessel and the inside wall was made from a UV reflector such as polished aluminum. The reaction was discontinued when the chlorine dioxide
15 concentration reached ten percent weight and the entire reaction product was removed from the reaction space. Ten percent was the upper limit chosen due to explosive properties of chlorine dioxide.

20 Similarly in Patent No. 4,877,500 to Callera, mixtures of chlorine and oxygen gas and aqueous solutions of sodium hypochlorite were photochemically converted to chlorine dioxide. As in the earlier Callera patent, the solution was held within the tubular vessel until the maximum concentration of chlorine dioxide reached ten percent. Afterwards, the entire reaction contents containing
25 chlorine dioxide were removed and conveyed to their place of use. In the photochemical reactions of chlorine and oxygen, explosions were reported to have occurred in two instances.

30 Improvements in safety of photochemical methods were reported by Simpson in US Patent No. 6,171,558. A means is described for positioning a UV bulb in a container of aqueous chlorite. The aqueous chlorite is circulated through a circulation tube by an air or gas sparge. This also effectively removes chlorine

dioxide and thus reduces the safety hazardous associated with its accumulation in solution.

While considerably improving upon the safety of the prior photochemical
5 methods the following limitations are still imposed:

- (1) The prior art requires additional air moving system to generate a gas sparge.
- 10 (2) The prior art was conducted in fragile quartz tubes and aspirators.
- (3) The prior art requires a circulation tube in proximity to the ultraviolet bulb to conduct the chlorite precursor across the field of ultraviolet radiation.
- 15 (4) The prior art production of chlorine dioxide cannot be directly regulated by controlled addition of chlorite precursor. The prior art production of chlorine dioxide must be controlled by bulb intensity and gas sparge rate.
- 20 (5) The scale-up of the prior art device is difficult. The chlorine dioxide production rate also decreases as the chlorite is exhausted

Chlorine dioxide has the potential for increased use in a variety of commercial
25 and industrial applications. The apparatus for its generation would ideally be safe, economical, easy-to-use, and not require storage of hazardous ingredients. A clear and compelling need exists for a device that produces chlorine dioxide while fulfilling the above criteria.

30

SUMMARY OF THE INVENTION

Objectives of the present invention include provides apparatus and methods for generating chlorine dioxide in an air stream or dissolved in a liquid stream on

demand that solve the numerous problems of the prior art described herein above.

The objectives of the present invention are met by a chlorine dioxide generator comprising:

a reaction vessel constructed and arranged to contain a chlorine dioxide generating solution that forms chlorine dioxide upon exposure to UV light;

a source of UV light constructed and arranged to provide UV light to said reaction vessel such that when said generator is operating UV light contacts the chlorine dioxide generating solution when present within the reaction vessel to produce activated solution containing chlorine dioxide;

at least one solution inlet associated with said reaction vessel constructed and arranged to allow chlorine dioxide generating solution or an active agent that forms chlorine dioxide upon exposure to UV light to flow into said reaction vessel during operation of said generator;

at least one solution outlet associated with said reaction vessel constructed and arranged to allow spent activated solution to flow out of said reaction vessel during operation of said generator;

at least one chlorine dioxide exit associated with said reaction vessel constructed and arranged to allow chlorine dioxide gas to exit said reaction vessel during operation of said generator;

a gas permeable structure constructed and arranged to allow chlorine dioxide gas to exit said reaction vessel during operation of said generator by passing through said structure and to contain the chlorine dioxide generating solution and activated solution in said reaction vessel when present in the reaction vessel;

a source of ultrasonic vibrations constructed and arranged to vibrate the activated solution and facilitate removal of chlorine dioxide from the activated solution during operation of said generator; and

evacuating structure in communication with the reaction vessel to facilitate continuous evacuation of chlorine dioxide from said reaction vessel during operation of said generator.

The objectives of the invention are also met by a method of making chlorine dioxide on demand comprising:

- 5 exposing a chlorine dioxide generating solution to UV light to form an activated solution containing chlorine dioxide in a reaction vessel;
- agitating said activated solution using a source of ultrasonic vibrations to drive chlorine dioxide from said activated solution;
- using a gas permeable structure to separate said chlorine dioxide from said activated solution;
- 10 facilitating the evacuation of chlorine dioxide from the reaction vessel using reduced pressure from a water driven eductor or air flow; and
- forming an air flow stream containing chlorine dioxide or an aqueous stream containing dissolved chlorine dioxide.

- 15 The objectives of the invention are met by a chlorine dioxide generator and air cleanser comprising:

- a reaction vessel constructed and arranged to contain a chlorine dioxide generating solution that forms chlorine dioxide upon exposure to UV light;
- a source of UV light constructed and arranged to provide UV light to said
- 20 reaction vessel such that when said generator is operating UV light contacts the chlorine dioxide generating solution when present within the reaction vessel to produce activated solution containing chlorine dioxide;
- a column in communication with said reaction vessel having at least one air inlet and at least one air outlet;
- 25 dispersing structure in communication with said column for dispersing activated solution in said column during operation;
- a pump for transferring activated solution from said reaction vessel to said dispersing structure;
- at least one liquid outlet in said column constructed and arranged to allow
- 30 activated liquid leaving the column during operation to transfer back to said reaction vessel; and
- a air-moving device to provide an air stream through said column.

The objectives of the invention are further met by a chlorine dioxide generator for providing a stream of chlorine dioxide dissolved in a liquid solvent comprising:

5 a reaction vessel constructed and arranged to contain a chlorine dioxide generating solution that forms chlorine dioxide upon exposure to UV light having at least one vessel air inlet and at least one vessel air outlet;

a source of UV light constructed and arranged to provide UV light to said reaction vessel such that when said generator is operating UV light contacts the chlorine dioxide generating solution when present within the reaction vessel to produce activated solution containing chlorine dioxide;

10 a source of ultrasonic vibrations constructed and arranged to vibrate the activated solution and facilitate removal of chlorine dioxide from the activated solution during operation of said generator;

a column in communication with said reaction vessel having at least one column air inlet, at least one column air outlet, at least one liquid input and at least one liquid outlet;

15 a air-moving device in communication with the vessel air inlet to provide an air stream through said reaction vessel during operation to form an air stream containing chlorine dioxide, the vessel air outlet being in communication with the column air inlet.

20 dispersing structure in communication with said liquid inlet for dispersing solvent in said column such that the solvent contacts the air stream containing chlorine dioxide during operation to form solvent containing dissolved chlorine dioxide; and

25 at least one liquid outlet in said column constructed and arranged to allow solvent containing dissolved chlorine dioxide to exit the column during operation.

The objectives of the invention are also met by a method of cleaning an air stream comprising:

30 exposing a chlorine dioxide generating solution to UV light to form an activated solution containing chlorine dioxide in a reaction vessel;

transferring the activated solution to a column in communication with said reaction vessel;

flowing an air stream through said column to contact said activated solution and form a cleaned air stream leaving said column.

The objectives of the invention are further met by a method of providing a liquid
5 stream of chlorine dioxide comprising:

exposing a chlorine dioxide generating solution to UV light to form an activated solution containing chlorine dioxide in a reaction vessel;

agitating said activated solution using a source of ultrasonic vibrations to drive chlorine dioxide from said activated solution;

10 flowing an air stream through said vessel to form an air stream containing chlorine dioxide;

transferring the air stream containing chlorine dioxide to a column in communication with said reaction vessel; and

supplying a solvent into said column such that it contacts the air stream
15 containing chlorine dioxide to form a solvent containing chlorine dioxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a side view of a chlorine dioxide generator according to the
20 present invention;

Fig. 2 illustrates a side view of UV bulbs and a reaction vessel according to the present invention;

Fig. 3 illustrates a 3 is a top view of UV bulbs in relation to ultrasonic plates according to the present invention;

25 Fig. 4 illustrates a side view of a reaction vessel, UV bulbs and ultrasonic discs according to the present invention;

Fig. 5 illustrates a view of a reaction vessel having three liquid line attachments;

Fig. 6 illustrates a view of an air stream embodiment according to the present invention.

30 Fig. 7 illustrates a combined UV reaction vessel according to the present invention;

Fig. 8 illustrates an embodiment of a UV reaction vessel and air cleanser; and

Fig. 9 illustrates an embodiment of a UV reaction vessel for providing a liquid

chlorine dioxide stream.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

5 The present invention relates to a novel chlorine dioxide generator. The present invention also relates to a novel method to produce and simultaneously recover chlorine dioxide on demand by exposing a chlorine dioxide generating solution to UV light in a chlorine dioxide generator.

10 The chlorine dioxide generating solution comprises at least one active agents that forms chlorine dioxide upon exposure to UV light, which is dissolved or dispersed in an aqueous medium. Examples of chlorine dioxide generating solutions include, but are not limited to active agents comprising chlorites, such
15 as alkali metal chlorites or alkaline earth chlorites, chlorine, hypochlorites, trichloro isocyanuric acid, and/or salts of organic chlorine donors, such as sodium dichloroisocyanate (NaDDC), which are dissolved or dispersed in an aqueous medium. The aqueous medium can comprise water, tap water, reprocessed water, recycled water, water containing desired additives, and recycled spent
20 activated solution. Preferably, the chlorine dioxide generating solution comprises sodium chlorite as the active agent. Technical grade sodium chlorite can be utilized if desired. When sodium chlorite is utilized, preferably it is present in an amount of from about 1 to about 5 % by weight.

25 Once the chlorine dioxide generating solution is exposed to UV light, it forms an activated solution containing chlorine dioxide and also usually contains chloride ions, chlorate ions, and other oxychloro species dissolved or dispersed in the aqueous medium.

30 The chlorine dioxide generating solution and activated solution are contained in a reaction vessel. The reaction vessel can be formed from any suitable material that is resistant to the chlorine dioxide generating solution, activated solution, chlorine dioxide and any other additives utilized. Examples of reaction vessel materials include glass, quartz, plastic, and/or metals.

The reaction vessel can be any shape or size as desired. Preferably, the reaction vessel is shaped so that readily available cylindrical UV bulbs can easily be mounted within the reaction vessel.

5

The reaction vessel contains at least one chlorine dioxide exit through which generated chlorine dioxide can be continuously evacuated from the reaction vessel during operation of the chlorine dioxide generator. The reaction vessel also preferably contains at least one solution inlet and at least one solution outlet
10 through which the level and/or replenishment of chlorine dioxide generating solution can be adjusted in the reaction vessel by adding new chlorine dioxide generating solution through the solution inlet and by removing spent activated solution having chlorine dioxide removed therefrom through the solution outlet. Since the fresh chlorine dioxide generation solution and activated solution are
15 intermixed, some chlorine dioxide generating solution may also be discarded through the solution outlet as well. The flow of fresh chlorine dioxide generation solution into the solution inlet can be controlled by a metering pump, a solenoid operated valve with a timer to meter a carefully controlled rate of chlorine dioxide generating solution, or other controls. Alternatively, the aqueous medium and
20 the active agent that forms chlorine dioxide upon exposure to UV light can be added to the reaction vessel separately through separate solution inlets with the flow of each being independently controlled so that the chlorine dioxide generation solution is formed within the reaction vessel. The flow of spent activated solution through the solution outlet can be controlled using a solenoid
25 valve and float switch, or other controls as desired. The reaction vessel can also contain an overflow line to prevent overfilling of the reaction vessel with chlorine dioxide generating solution and/or aqueous medium.

UV light sources are now well known. Any suitable UV light source can be used
30 in the present chlorine dioxide generator. For example, one or more UV bulbs can be used as the source of UV light. The UV bulbs preferably run along most of the width or length of the reaction vessel illuminating the entire contents with

UV light when the generator is operating. The UV bulbs are preferably positioned inside the reaction vessel to maximize exposure of the chlorine dioxide generating solution. Cylindrical UV bulbs can be used. Low pressure mercury vapor bulbs are suitable. The amount of UV light is controlled by a UV controller. Preferably, the predominate UV light wavelength is less than 260 nm to reduce adsorption of UV light by the chlorine dioxide, and more preferably the UV light wavelength utilized is 254 nm. Suppliers of suitable UV bulbs include Cathodeon Ltd., Hellma USA, and Heraeus Inc.

Sources of ultrasonic vibrations are now well known. Any suitable ultrasonic device can be utilized in the present invention to agitate the activated solution during production of chlorine dioxide. For example, a series of ultrasonic piezoelectric plates can be installed along the middle of the reaction vessel. Preferably, ultrasonic piezoelectric plates are mounted inside of the reaction vessel to directly contact the activated solution. Without being bound by any theory, it is believed that the ultrasonic discs translate electrical power into high frequency ultrasonic vibrations that produce an ultrasonic wave in the activated solution. The ultrasonic wave rapidly drives dissolved or dispersed chlorine dioxide from the activated solution, which can be in the form of bubbles. Preferably, the piezoelectric plates vibrate at ultrasonic frequency from 1.6 MHz to 2.5 MHz. Other ultrasonic devices operating at lower frequencies, such as in the kHz range, or even higher frequencies, can also be used to drive the chlorine dioxide gas from the solution, as desired for the particular application. Suppliers of suitable ultrasonic piezoelectric plates include American Piezo Ceramics, Blue Wave Ultrasonics, Piezo Technologies, Piezo Solutions, Omegasonics, and Ultrasonic Power Corp (UPC).

Before the chlorine dioxide is evacuated from the reaction vessel through the chlorine dioxide exit, it passes through a gas permeable structure inside of the reaction vessel. If desired, the gas permeable structure can be located after the chlorine dioxide exit, although that arrangement is not preferred. Gas permeable structures are now well known. A gas permeable structure should be selected

which is capable of containing the chlorine dioxide generating solution and activated solution within the reaction vessel but which allows the chlorine dioxide gas to pass therethrough. Suitable gas permeable structures are commercially available.

5

Evacuation of the produced chlorine dioxide from the reaction vessel is facilitated by using evacuation structure. Examples of evacuation structure include an air stream and reduced pressure. Evacuation of chlorine dioxide from the reaction vessel should be simultaneous with the production of chlorine dioxide to minimize exposure of chlorine dioxide to UV light and to provide on demand chlorine dioxide.

10

In one embodiment, the gas permeable structure and chlorine dioxide exit are connected to a water-driven venturi eductor that reduces the pressure in the reaction vessel thereby facilitating the flow of free chlorine dioxide from the activated solution and through the structure into an aqueous flow line. Chlorine dioxide is highly soluble in water and immediately forms an aqueous chlorine dioxide solution in the aqueous flow line. The chlorine dioxide solution can then be piped to its point of use. The type of water used can be as desired for the particular application. For example, tap water, process water, recirculating wash water, and recycled water can be used as desired. If tap water is utilized, a water tap connector can be mounted on the eductor so that it can be easily connected to tap water. For example, the eductor can be run to provide concentrations chlorine dioxide dissolved in the water, such as about 1 to about 3000 parts per million (mg/liter), as desired for the particular application.

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If gaseous chlorine dioxide is preferred, instead of using the water-driven venturi eductor a small fan can be used to drive off the chlorine dioxide produced in the reaction vessel and form an air stream containing the chlorine dioxide. The fan can be mounted so that it blows air into the reaction vessel and across the surface of the activated solution or so that it creates a reduced air pressure in the reaction vessel such that air flows into the reaction vessel and across the surface

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of the activated solution. Small amounts of water vapor droplets may also be expelled through the exit tubes that project outwards from the reaction vessel. If desired, when using an air stream the gas permeable structure can be excluded.

The air stream mixed with chlorine dioxide produces a dilute mixture of air, chlorine dioxide, and water vapor that can be piped to its point of use. The concentration of chlorine dioxide can be accurately controlled, for example, by controlling the fan speed and/or the amount of chlorine dioxide generating solution added to the reaction vessel. The concentration of chlorine dioxide in the air stream leaving the generator is usually about 5 to about 100 ppm, but can be selected as desired for the particular application.

The concentration and amount of chlorine dioxide can be continuously adjusted by adjusting the flow of the chlorine dioxide generating solution, the intensity of the UV light, the fan speed if present, and amount of vacuum supplied by the eductor if present. Preferably, the concentration and amount of chlorine dioxide is adjusted by adjusting the flow of chlorine dioxide generating solution into the reactor. If desired, chlorine dioxide sensors can be utilized in combination with a computer and/or feedback from an apparatus using the chlorine dioxide to control the production of chlorine dioxide. Other sensors, such as pollutant sensors like hydrogen sulphide, can also be utilized in the control of the chlorine dioxide.

Preferably, the controls, source of UV light, source of ultrasonic vibrations, fan, metering pump and any other electrical devices utilized operate on 110V or 220V.

The invention will now be described with reference to the attached Figures. Fig. 1 is a schematic drawing showing chlorine dioxide generator. The reaction vessel (20) houses two or more cylindrical UV bulbs (23). The UV bulbs are connected to the reaction vessel (20) by means of a threaded mount (24). A series of ultrasonic piezoelectric plates (22) are installed in the bottom of the reaction vessel (20) in a manner so that the piezoelectric plates come into direct

contact with the activated solution inside the reaction vessel (20) during operation. A gas permeable structure (21) retains the activated solution within the reaction vessel (20) but allows gaseous chlorine dioxide to pass through and out the chlorine dioxide exit (27).

5

Fig. 2 is a perspective drawing showing the placement of the UV bulbs (23) within the reaction vessel (20). Fig. 3 is a top view illustrating the arrangement of the UV bulbs (23) in relation to the ultrasonic piezoelectric plates (22). The UV bulbs are fastened to the reaction vessel by a threaded mount (24) and by bulbs (26).

10 The threaded mount (24) allows the easy removal and replacement of the UV bulbs. Fig. 4 shows a side view of the reaction vessel (20) and orientation of UV bulbs (23) and ultrasonic discs (22).

Fig. 5 shows the outside of the reaction vessel with three liquid line attachments.

15 An active agent line (30) supplies the sodium chlorite or other active agent to the reaction vessel (20) through an active agent inlet (40). The active agent can be pumped into the reaction vessel (20) using a standard metering pump (39). The metering pump is preferably operated using 110V or 220V (43). The active agent is stored in a container (45) and is supplied to the metering pump (39) using
20 supply line (44). The liquid level is maintained using a float switch (37) connected to a solenoid valve (36). When the liquid level drops, the float switch (37) activates the solenoid valve (36) which allows water to enter the reaction vessel (20) through water inlet (41) until a desired liquid level is reached and the float switch (37) shuts off the solenoid valve (36). The reaction vessel (20) is
25 equipped with a solution outlet (32) to remove spent reactants and can be controlled with a solenoid valve (42). These devices keep the liquid level in the reaction vessel at a constant depth and volume. An overflow outlet (34) is also
attached for additional safety and control. The overflow outlet (34) and solution
outlet (32) merge to form a waste line (38), where spent reactants can be
30 disposed as required by law. If a fan is utilized, as shown in Fig. 6, the water may have to be replenished more often due to increased evaporation and water droplet removal.

Fig. 6 illustrates an alternative embodiment in which the chlorine dioxide is maintained in the gaseous form, i.e. not dissolve it in an aqueous stream. A device for projecting a gaseous stream of chlorine dioxide is shown in attached pictures of reaction vessel (20). In this embodiment, a fan (50) blows air into the reaction vessel (20) through air inlet (51) which drives off the chlorine dioxide produced in the reaction vessel (20) and exits through the chlorine dioxide exit (27). While a gas permeable structure (21) is shown in Fig. 6, the generator (1) can be run without the use of the gas permeable structure (21). If no gas permeable structure (21) is utilized, small amounts of water vapor droplets may also be expelled through the chlorine dioxide exit (27).

In some cases, especially if a larger flow of chlorine dioxide generating solution is required, it is preferable to separate the photoactivation of the chlorine dioxide generation solution to form activated solution and recovery of chlorine dioxide from the activated solution into two steps. This means that the photocatalytic reaction of the chlorine dioxide generating solution in the reaction vessel should be complete before entering a separate separation chamber and being agitated by the piezoelectric plates. This would reduce the amount of chlorine dioxide generating solution present with the spent reactants being discarded, thereby increasing yield and efficiency. Thus, in this embodiment, the source of ultrasonic vibrations, chlorine dioxide exit, solution exit and evacuation structure as described herein above are located in the separation chamber, not the reaction vessel.

There are several configurations possible for the UV bulb and flow path of the chlorine dioxide generating solution. UV water sterilization systems utilize a helical or serpentine path of water around and proximate to a low power mercury bulb. It has now been found that such a configuration could be used to irradiate the chlorine dioxide generation solution according to the present invention to produce chlorine dioxide.

It has also now been found that UV microwave powered electrodeless bulbs, such as those disclosed in U.S. patent No. 5,614,151, the complete disclosure of which is incorporated herein by reference, offer several distinct advantages to conventional low pressure mercury vapor bulbs. The bulb operates using
5 microwave radiation to energize a UV-emitting bulb. Since the bulb does not use electrodes, the bulb can operate as low, medium, or high pressure bulbs, and bulb life is extended almost indefinitely. This type of bulb has demonstrated low pressure mercury wavelengths at about 10 times the power of conventional systems. Further, since the constraints of electrodes do not apply, the bulbs can
10 be made virtually in any shape.

Using the electrodeless bulb design, I have now combined the UV bulb, reaction vessel and flow path of the chlorine dioxide generating solution to be housed together in a single combined UV reaction vessel. This is a distinct advantage in
15 that it increases the surface area and exposure of the chlorine dioxide generating solution to the UV source. It also simplifies the reaction vessel design and reduces its complexity and cost considerably.

Fig. 7 shows a combined UV reaction vessel (50) in which the chlorine dioxide
20 generating solution enters the inner annulus (51) of the UV reaction vessel (50) at (52) and is conducted along the UV emitting surface (53) of the UV bulb (54). The UV bulb (54) is preferably an electrodeless bulb design containing a mixture of argon and mercury vapor. While argon and mercury vapor are shown, other noble gases can be used instead of or in addition to argon. The turbulence
25 created by the flow of the chlorine dioxide generating solution ensures that fresh chlorine dioxide generating solution is always in contact with the UV emitting surface (53). Activated solution exiting the inner annulus (51) at (55) contains aqueous chlorine dioxide and also usually contains chloride ions, chlorate ions, and other oxychloro species. The activated solution can either be used
30 immediately since it contains chlorine dioxide or conducted to a separation chamber and agitated using a source of ultrasonic vibrations and evacuation structure to drive the chlorine dioxide from the activated solution leaving the other

reactants in an ionic solution. An air stream or aqueous stream of chlorine dioxide can be formed using the evacuation structure as described herein above with reference to other embodiments.

- 5 If the activated solution containing chlorine dioxide is used prior to separation of the chlorine dioxide, additional additives can be mixed with the chlorine dioxide generating solution prior to photoactivation. Examples of additives may be surfactants, water softening agents, dispersants, solvents, wetting agents. If sodium chlorite is used as the active agent, conventionally, these materials have
10 to be added or mixed with acidified sodium chlorite solution. The low pH of such acidified chlorite solutions may preclude adding many types of additives. The ability to add these agents prior to the UV initiated reaction and formation of chlorine dioxide allows the production of agents useful in a variety of commercial applications such as hard surface cleaning, sanitizing equipment and surfaces,
15 and oil and water well injection.

In certain cases it is useful to treat an air stream with chlorine dioxide. This is accomplished by circulating the chlorine dioxide generation solution through a packed column which provides for liquid / gas contact, as shown in Fig. 8. The
20 chlorine dioxide produced in the UV activation chamber is then available to neutralize chemical or biological contaminants in the air stream.

Chemical contaminants include but are not limited to hydrogen sulfide and reduced organic sulfur compounds such as mercaptans and thiols. The alkaline
25 pH of the chlorine dioxide generating solution also reacts and removes acid gases. Biological contaminants include but are not limited to bacteria, spores, viruses, molds, fungi, etc. Airborne particulate matter is also removed in the packed column.

- 30 An air cleansing apparatus (96) is shown in Fig. 8. In this apparatus (96) the activation chamber or reaction vessel (60) is similar to the main embodiment described above in that the UV bulbs (61) are mounted in a horizontal

orientation. The vessel (60) can be of any shape or volume as desired for the particular application. An example of a suitable size is about 20 liters. A chlorine dioxide generating solution tank (62) is connected to an solution inlet (91). The amount of chlorine dioxide generating solution supplied from the tank (62) can be controlled by metering structure (90), such as a metering pump or solenoid-operated valve to vessel (60). The chlorine dioxide generating solution (64) upon exposure to the ultraviolet radiation from the UV bulbs (61) is photochemically oxidized to form an activated solution containing chlorine dioxide. The activated solution in this embodiment may be mixed with chlorine dioxide generating solution in this embodiment. The reaction primarily occurs at or near the surface of the bulbs (61). A preferred chlorine dioxide generating solution in this embodiment comprises aqueous sodium chlorite at a concentration of about 1 to about 20% by weight.

The produced chlorine dioxide present in the activated solution is quickly removed from the vessel (60) by a circulating submersible water pump (63). This avoids the decay of chlorine dioxide by UV and visible light produced by the bulbs (61). The wavelength of UV that decays chlorine dioxide is mostly greater than 300 nm. The vessel (60) is also equipped with a drain (92) to periodically remove spent chlorine dioxide generating solution (64). Preferably, the pump (63) and solution inlet (91) are on opposite sides of the vessel (60) to reduce the amount of fresh chlorine dioxide generating solution picked up by pump (63) and mixed with the activated solution.

The vessel (60) should be fitted with a cover to prevent evaporation of chlorine dioxide from the circulated chlorine dioxide generating solution. The circulating chlorine dioxide concentration in the activated solution can be maintained at any desired level, such as between 1 – 5 ppm, by metering the flow of chlorine dioxide generating solution to the vessel (60). Preferably, the chlorine dioxide can be measured using an optional photo-spectrometer (94). If high chemical loads are present in the airstream entering the apparatus (96) greater circulating concentrations of chlorine dioxide may be required.

A submersible water pump (63) is present in the vessel (60). The function of the water pump (63) is to circulate the mixture of activated solution to dispersing structure (65), such as spray nozzles, located at the top of the column (66). The activated solution can be dispersed in the to the column (66) in any desired manner an, such as by allowing the activated solution to pour over the packing material (69). However, the use of spray nozzles (65) is preferred. The column (66) can be situated above the vessel (60) to provide gravity feed of the activated solution from the column (66) to the reaction vessel (60).

The column (66) can be any shape or dimension as desired for the particular application. An example of a suitable size is a rectangular shape of about 2 feet wide by 2 feet deep by 3 feet high. The column (66) is fitted with at least two openings, air inlet (67) and air outlet (68). At least one air inlet (67) opening near the bottom of the column (66) allows the passage of an air stream to move in and upwards through the column (66) in counter current direction to the flow of the activated solution containing chlorine dioxide. At least one air outlet (68) opening near the top of the column (66) allows the air stream to flow out of the column (66). Preferably, the outlet (68) and inlet (67) are located on opposite sides of the column (66). By using a counter current flow, the transfer of chlorine dioxide from the activated solution to the air stream is maximized.

The column (66) is preferably filled with a high surface area packing material (69) to maximize contact between the air stream and the activated solution. An example of a suitable packing material is NuPac (55 square ft per cubic ft., manufactured by Lantec Products, Inc.). However, any suitable inert packing material can be used, such as beads, saddles, cubes, pads, or irregular shaped pieces of plastic, ceramic, metal, or glass. This counter current flow of the air stream and activated solution provides a sufficient concentration of chlorine dioxide to neutralize airborne contaminants. A plurality of liquid outlets (70), such as perforations perforated along the bottom of the column (66), allow the activated solution to drain back into the vessel (60). Most of the chlorine dioxide

present in the activated solution will be transferred to the air stream in the column (66).

The spray nozzles (65) mounted at the top of the column (66) distribute the activated solution evenly throughout the column (66) and if packing material (69) is present to evenly distribute the activated solution over the upper surface of the packing material (69) to provide an even flow through the column (66). A mist eliminator pad (71) is disposed above the spray nozzles to remove particulate amounts of activated solution from the air stream. A screen (97) can be used to retain the packing material (69) in the column (66). The air stream can be provided by a blower, fan, or any air-moving device (98) as desired. The air-moving device should supply an adequate pressure to force the air through the packed column.

The utilization of dissolved chlorine dioxide produced in this embodiment is unique and non-obvious. Chlorine dioxide exists as a true gas in the activated solution and is therefore available for the neutralization reactions mentioned above. The activated solution also can contain unreacted chlorite ions and photochemical reaction products such as chloride ions and various oxy-chloro species.

In the current embodiment, it is not necessary to separate the produced chlorine dioxide from the activated solution containing reactants prior to treatment of the air stream. The prior art using ultraviolet radiation teaches methods of separating and removing produced chlorine dioxide from the reaction products. There is no mention in the prior art with regard to directly employing the activated solution in the desired application.

The air stream need only contact chlorine dioxide in the column to effect decontamination or disinfection. In addition, only a small concentration, such as from about 1 to about 5 ppm, of chlorine dioxide is required in the circulating activated solution. The low circulating concentration of chlorine dioxide substantially improves upon the safety margin of prior art chemical oxidation gas

scrubbing methods.

- It is conceivable in this example to implement feedback regulation using an optional aqueous chlorine dioxide sensor (95). As the chlorine dioxide is consumed in the packed column, a drop in the chemical potential of the chlorine dioxide generating solution in the vessel (60) could be easily measured and relayed to a controller (99) for the chlorine dioxide generating solution metering structure (90). This structure is useful in optimizing the chlorine dioxide generating solution in circumstances requiring high decontamination loads such as in gas scrubbers. This aspect of the invention is distinct and stands in contrast to standard chemical feedback systems, which directly measure the gaseous pollutant concentration. Analytical methods for measurement of gases are more complex and expensive compared with aqueous methods.
- This embodiment shown in Fig. 8 describes in a general way a method of generating chlorine dioxide in a circulating aqueous stream of water that is flowed counter current through an air / liquid contactor (column 66). This basic design concept can be incorporated into any system utilizing an air moving device and an air / liquid contactor. Practical examples of such systems include gas scrubbing devices, air washers, evaporative coolers, and humidifiers. While the prior art teaches many different types of scrubbing devices, air washers, evaporative coolers, and humidifiers, the prior art does not teach incorporating chlorine dioxide into any of these systems.
- Fig. 9 illustrates an apparatus (74) in which chlorine dioxide gas produced in the current invention can also be dissolved into a stream of water. The aqueous chlorine dioxide solution can then conveyed to any point of use. Alternatively a re-circulating stream of water, such as process water from a poultry chill tank, may be treated by chlorine dioxide in the same manner.
- The activation chamber or reaction vessel (83) is equipped with UV bulbs (82) as in the main embodiment. The chlorine dioxide generating solution (72) present in

tank (84) is circulated through the vessel (83) and back to tank (84) by means of a submersible water pump (73). The photochemical reaction occurs at the surface of the bulbs (82). A preferred chlorine dioxide generating solution in this embodiment comprises about 5% by weight of sodium chlorite in water.

5

In this embodiment the limiting variable in the photochemical reaction is the surface area of the UV bulbs, not the concentration of chlorine dioxide generating solution, such as sodium chlorite, as in the main embodiment. The volume of the chlorine dioxide generating solution (72) in tank (84) is preferably large compared with the volume of chlorine dioxide generating solution in vessel (83). The tank holding the chlorine dioxide generating solution is usually between 20 – 1000 liters, where as the activation chamber is generally between 1 – 5 liters. The photochemical reaction will proceed as long as there is sufficient chlorine dioxide generating solution. As described above, when the chlorine dioxide generating solution is exposed to UV light, it forms activated solution containing reaction products and chlorine dioxide. As the apparatus is run, the amount of activated solution mixed with chlorine dioxide generating solution in the tank (72) will increase. This is similar to the prior art of Simpson (US 6,171,558) who found that the production of chlorine dioxide was not dependant upon chlorite ion concentration and was constant over an extended time period. However, the production of chlorine dioxide will decline gradually as the concentration of chlorite decreases below about 100 ppm.

The chlorine dioxide produced in vessel (83) can be quickly separated from the activated solution by the ultrasonic discs (75) located along the bottom of the vessel (83). The activated solution is vibrated at ultrasonic frequencies, such as 1.5 MHz, to release the produced chlorine dioxide gas.

An air-moving device (76) provides an air stream to the vessel (83) through air inlet (88) and air outlet (89) to propel the chlorine dioxide gas from vessel (83) through a mist eliminator pad (77) and air inlet (87) into a packed column (78). The mist eliminator pad (77) removes small particles of liquid, which are

vaporized by the ultrasonic discs (75). The trapped liquid then flows back into the activation vessel (83).

The packed column (78) acts as a liquid/gas contactor, where the chlorine dioxide gas is dissolved into a liquid solvent, such as water. Chlorine dioxide gas is highly soluble in water and will be removed from the air stream flowing through the packed column (78). The column (78) is preferably filled with the high surface area packing material (79) to maximize contact between the liquid solvent and the chlorine dioxide gas. A liquid inlet (85) supplies liquid solvent to dispersing structure (80), such as spray nozzles, mounted at the top of the column (78) to provide even flow of the liquid solvent through the column (78). Any dispersing structure (80) can be used to disperse the solvent in the column (78), however, the use of spray nozzles (80) is preferred. The dissolved chlorine dioxide then exits the packed column (78) through the liquid outlet (81). The air stream exits the packed column (78) at air exit (86).

Unexpected advantages of the present invention include but are not limited to:

- (1) Pure aqueous chlorine dioxide in solution or an air stream can be produced with no dissolved solids.
- (2) Chlorine dioxide solution has a neutral pH (7).
- (3) Corrosive properties of chlorine dioxide are reduced.
- (4) Chlorine dioxide is rapidly transported away from reactants to minimize or obviate undesirable side reactions.
- (5) A high degree of control in chlorine dioxide production is provided, with a large turndown ratio.
- (6) Technical grade chlorite can be used, and highly purified chlorite not required.
- (7) Pure solutions of chlorine dioxide do not undergo unwanted side reactions.
- (8) A single precursor system can be used and additional reagents are not required.

- 5
- (9) The cost, storage and liability of additional hazardous reagents is avoided.
 - (10) Complex feedback and control systems not required.
 - (11) Production and separation of chlorine dioxide can be conducted in single step.
 - (12) Gaseous or aqueous chlorine dioxide can be produced as desired on demand.
 - (13) The present invention allows commercially useful solutions, such as hard surface cleaning agents and sanitizers, to be produced in a single step.
- 10

The use of the ultrasonic vibrations provides the following unexpected advantages:

- 15
- 1) Separation of chlorine dioxide from reactants to avoid UV degradation and side reactions with spent reactants.
 - 2) Turbulence in the chlorine dioxide generating solution since fresh sodium chlorite must constantly come into contact with the UV light. UV light does not penetrate deeply into the chlorine dioxide generating solution as the sodium chlorite strongly absorbs the UV light. Therefore turbulence is necessary to expose fresh solution for UV activation.
- 20
- 3) Avoids having to use an air sparge that requires an air pump or compressor, such as in U.S. patent No. 6,171,558 (Simpson).
 - 4) Provides a means of separating chlorine dioxide without dilution of air.
- 25
- 5) Avoids using the circulating tube described in the prior art (Simpson 2001) to remove the chlorine dioxide bubbles that form on the surface of the lamp.
- 30
- 6) The turbulence generated by the ultrasonic vibrations prevents the formation of small micro-bubbles of chlorine dioxide on the lamp and simultaneously sweeps chlorine dioxide away from the

chlorine dioxide generating solution.

- 7) The ultrasonic transducers also produce a fine mist (usually about one micron sized particles) of chlorine dioxide solution. This can be directly employed in some applications that require surface or air stream disinfection.

5

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

10

CLAIMS:

1. A chlorine dioxide generator comprising:
 - a reaction vessel constructed and arranged to contain a chlorine dioxide
 - 5 generating solution that forms chlorine dioxide upon exposure to UV light;
 - a source of UV light constructed and arranged to provide UV light to said reaction vessel such that when said generator is operating UV light contacts the chlorine dioxide generating solution when present within the reaction vessel to produce activated solution containing chlorine dioxide;
 - 10 at least one solution inlet associated with said reaction vessel constructed and arranged to allow chlorine dioxide generating solution or an active agent that forms chlorine dioxide upon exposure to UV light to flow into said reaction vessel during operation of said generator;
 - at least one solution outlet associated with said reaction vessel
 - 15 constructed and arranged to allow spent activated solution to flow out of said reaction vessel during operation of said generator;
 - at least one chlorine dioxide exit associated with said reaction vessel constructed and arranged to allow chlorine dioxide gas to exit said reaction vessel during operation of said generator;
 - 20 a gas permeable structure constructed and arranged to allow chlorine dioxide gas to exit said reaction vessel during operation of said generator by passing through said structure and to contain the chlorine dioxide generating solution and activated solution in said reaction vessel when present in the reaction vessel;
 - 25 a source of ultrasonic vibrations constructed and arranged to vibrate the activated solution and facilitate removal of chlorine dioxide from the activated solution during operation of said generator; and
 - evacuating structure in communication with the reaction vessel to facilitate continuous evacuation of chlorine dioxide from said reaction vessel during
 - 30 operation of said generator.

2. A chlorine dioxide generator according to claim 1, wherein said

evacuating structure comprises a water-driven venturi eductor in communication with the chlorine dioxide exit and gas permeable structure which during operation of said generator the eductor provides an aqueous flow line and a reduced pressure in the reaction vessel to facilitate removal of free chlorine dioxide from the reaction vessel into an aqueous flow line forming an aqueous solution of chlorine dioxide.

3. A chlorine dioxide generator according to claim 1, wherein said evacuating structure comprises a fan in communication with the chlorine dioxide exit and gas permeable structure to facilitate removal of free chlorine dioxide from the reaction vessel into air flow forming a dilute mixture of chlorine dioxide and air during operation of said generator.

4. A chlorine dioxide generator according to claim 1, wherein said source of UV light is disposed within said reaction vessel.

5. A chlorine dioxide generator according to claim 1, wherein said source of UV light comprises at least one cylindrical UV bulb disposed within said reaction vessel.

6. A chlorine dioxide generator according to claim 1, wherein said source of UV light is external to said reaction vessel and said reaction vessel being at least partially constructed of a material that allows UV light to penetrate and contact the chlorine dioxide generating solution when present within the reaction vessel.

7. A chlorine dioxide generator according to claim 1, further comprising a metering pump connected to said solution inlet for controlling the flow of chlorine dioxide generation solution into said reaction vessel during operation of said generator.

8. A chlorine dioxide generator according to claim 1, further comprising a

solenoid valve and float switch to control the flow of spent chlorine dioxide generating solution from said reaction vessel during operation of said generator.

9. A chlorine dioxide generator according to claim 1, wherein said source
5 of ultrasonic vibrations comprises at least one ultrasonic piezoelectric plate disposed within said reactor.

10. A method of making chlorine dioxide on demand comprising:
exposing a chlorine dioxide generating solution to UV light to form an
10 activated solution containing chlorine dioxide in a reaction vessel;
agitating said activated solution using a source of ultrasonic vibrations to drive chlorine dioxide from said activated solution;
using a gas permeable structure to separate said chlorine dioxide from
said activated solution;
15 facilitating the evacuation of chlorine dioxide from the reaction vessel using reduced pressure from a water driven eductor or air flow; and
forming an air flow stream containing chlorine dioxide or an aqueous stream containing dissolved chlorine dioxide.

20 11. A method according to claim 10, wherein an aqueous steam containing dissolved chlorine dioxide is formed by using the water driven eductor.

25 12. A method according to claim 10, wherein an air stream containing chlorine dioxide is formed by using the air flow.

13. A method according to claim 10, wherein said chlorine dioxide generating solution comprises technical grade sodium chlorite.

30 14. A method according to claim 10, wherein the separation of chlorine dioxide from the activated solution is conducted in a separation chamber.

15. A method according to claim 10, wherein the exposure of said

chlorine dioxide generation solution to UV light is conducted in a combined UV reaction vessel having an electrodeless UV bulb through which the chlorine dioxide generation solution flows through and over to form said activated solution.

5

16. A chlorine dioxide generator comprising:

a reaction vessel constructed and arranged to contain a chlorine dioxide generating solution that forms chlorine dioxide upon exposure to UV light;

a source of UV light constructed and arranged to provide UV light to said reaction vessel such that when said generator is operating UV light contacts the chlorine dioxide generating solution when present within the reaction vessel to produce an activated solution containing chlorine dioxide;

at least one solution inlet associated with said reaction vessel constructed and arranged to allow chlorine dioxide generating solution or an active agent that forms chlorine dioxide upon exposure to UV light to flow into said reaction vessel during operation of said generator;

at least one solution outlet associated with said reaction vessel constructed and arranged to allow spent activated solution to flow out of said reaction vessel during operation of said generator;

at least one chlorine dioxide exit associated with said reaction vessel constructed and arranged to allow chlorine dioxide gas to exit said reaction vessel during operation of said generator;

a source of ultrasonic vibrations constructed and arranged to vibrate the activated solution and facilitate removal of chlorine dioxide from the activated solution during operation of said generator; and

a source of air flow in communication with the reaction vessel to facilitate continuous evacuation of chlorine dioxide from said reaction vessel during operation of said generator.

30

17. A reaction vessel comprising:

an electrodeless UV bulb constructed and arranged to be connected with a microwave source to generate UV light, the UV bulb having an outside surface

and an inner annulus through the UV bulb such that a chlorine dioxide generating solution flowing through the inner annulus can be exposed to UV light to produce aqueous chlorine dioxide.

5 18. The reaction vessel according to claim 18, further comprising a vessel case having an interior portion, the UV bulb being received in the interior portion such that the chloride dioxide generating solution can be exposed to UV light while passing through the inner annulus and at the outside surface of the UV bulb.

10

 19. A chlorine dioxide generator and air cleanser comprising:
 a reaction vessel constructed and arranged to contain a chlorine dioxide generating solution that forms chlorine dioxide upon exposure to UV light;
 a source of UV light constructed and arranged to provide UV light to said
15 reaction vessel such that when said generator is operating UV light contacts the chlorine dioxide generating solution when present within the reaction vessel to produce activated solution containing chlorine dioxide;
 a column in communication with said reaction vessel having at least one air inlet and at least one air outlet;
20 dispersing structure in communication with said column for dispersing activated solution in said column during operation;
 a pump for transferring activated solution from said reaction vessel to said dispersing structure;
 at least one liquid outlet in said column constructed and arranged to allow
25 activated liquid leaving the column during operation to transfer back to said reaction vessel; and
 a air-moving device to provide an air stream through said column.

 20. A generator according to claim 19, further comprising a packing
30 material present in said column.

 21. A generator according to claim 20, wherein the packing material

comprises one or more materials selected from the group consisting of NuPac, beads, saddles, cubes, pads, or irregular shaped pieces of plastic, ceramic, metal, or glass.

5 22. A generator according to claim 19, further comprising a mist eliminator disposed in the air stream path and constructed and arranged to reduce mist from exiting the column.

10 23. A generator according to claim 19, further comprising a chlorine dioxide generating solution tank and at least one solution inlet associated with said reaction vessel constructed and arranged to allow chlorine dioxide generating solution to flow from said chlorine dioxide generating solution tank into said reaction vessel during operation of said generator.

15 24. A generator according to claim 23, further comprising metering structure constructed and arranged for metering the amount of chlorine dioxide generating solution entering the reaction vessel through the solution inlet.

20 25. A generator according to claim 24, further comprising a chlorine dioxide sensor in the vessel, the chlorine dioxide sensor being connected to a controller for controlling the metering structure.

25 26. A generator according to claim 19, wherein the source of UV light comprises a plurality of UV bulbs mounted horizontally in said reaction vessel.

27. A generator according to claim 19, wherein the air input is located on a lower part of the column, the air output is located on an upper part of the column, and the nozzle is located in an upper part of the column so that the air stream and flow of activated solution are counter current through said column.

30 28. A generator according to claim 19, wherein the column is constructed and arranged so that the air stream and flow of activated solution through the

column are counter current.

29. A generator according to claim 19, wherein said generator is a gas scrubbing device, air washer, evaporative cooler, or humidifier.

5

30. A generator according to claim 19, wherein said dispersing structure comprises at least one spray nozzle.

31. A chlorine dioxide generator for providing a stream of chlorine dioxide
10 dissolved in a liquid solvent comprising:

a reaction vessel constructed and arranged to contain a chlorine dioxide generating solution that forms chlorine dioxide upon exposure to UV light having at least one vessel air inlet and at least one vessel air outlet;

a source of UV light constructed and arranged to provide UV light to said
15 reaction vessel such that when said generator is operating UV light contacts the chlorine dioxide generating solution when present within the reaction vessel to produce activated solution containing chlorine dioxide;

a source of ultrasonic vibrations constructed and arranged to vibrate the activated solution and facilitate removal of chlorine dioxide from the activated
20 solution during operation of said generator;

a column in communication with said reaction vessel having at least one column air inlet, at least one column air outlet, at least one liquid input and at least one liquid outlet;

a air-moving device in communication with the vessel air inlet to provide
25 an air stream through said reaction vessel during operation to form an air stream containing chlorine dioxide, the vessel air outlet being in communication with the column air inlet.

dispersing structure in communication with said liquid inlet for dispersing solvent into said column such that the solvent contacts the air stream containing
30 chlorine dioxide during operation to form solvent containing dissolved chlorine dioxide; and

at least one liquid outlet in said column constructed and arranged to allow

solvent containing dissolved chlorine dioxide to exit the column during operation.

32. A generator according to claim 31, further comprising a packing material present in said column.

5

33. A generator according to claim 32, wherein the packing material comprises one or more materials selected from the group consisting of NuPac, beads, saddles, cubes, pads, or irregular shaped pieces of plastic, ceramic, metal, or glass.

10

34. A generator according to claim 31, further comprising a mist eliminator disposed in the air stream path and constructed and arranged to reduce mist from entering the column.

15

35. A generator according to claim 31, further comprising a chlorine dioxide generating solution tank in communication with the vessel; at least one solution inlet associated with said reaction vessel constructed and arranged to allow chlorine dioxide generating solution to flow from said chlorine dioxide generating solution tank into said reaction vessel during operation of said generator; and at least one solution outlet associated with said reaction vessel constructed and arranged to allow chlorine dioxide generating solution to flow from said vessel to said chlorine dioxide solution generating tank during operation of said generator.

20

36. A generator according to claim 33, further comprising a pump for pumping chlorine dioxide generating solution from said vessel to said chlorine dioxide generating solution tank.

25

37. A generator according to claim 31, wherein the source of UV light comprises a plurality of UV bulbs mounted horizontally in said reaction vessel.

30

38. A generator according to claim 31, wherein the column is constructed

and arranged so that the flow of solvent and air stream containing chlorine dioxide are counter current.

39. A generator according to claim 31, wherein the column air input is
5 located on a lower part of the column, the column air output is located on an upper part of the column, and the nozzle is located in an upper part of the column so that the air stream containing chlorine dioxide and flow of solvent are counter current through said column.

10 40. A generator according to claim 31, wherein the dispersing structure comprises at least one spray nozzle.

41. A method of cleaning an air stream comprising:
exposing a chlorine dioxide generating solution to UV light to form an
15 activated solution containing chlorine dioxide in a reaction vessel;
transferring the activated solution to a column in communication with said reaction vessel;
flowing an air stream through said column to contact said activated
solution and form a cleaned air stream leaving said column.

20

42. A method according to claim 41, further comprising transferring activated solution from the column to said vessel.

43. A method according to claim 41, further comprising flowing the
25 activated solution and air stream through a packing material present in said column.

44. A method according to claim 43, wherein the packing material
comprises one or more materials selected from the group consisting of NuPac,
30 beads, saddles, cubes, pads, or irregular shaped pieces of plastic, ceramic, metal, or glass.

45. A method according to claim 41, further comprising using a mist eliminator disposed in the air stream path to reduce mist from exiting the column.

46. A method according to claim 41, further comprising flowing chlorine
5 dioxide generating solution from a chlorine dioxide generating solution tank to said vessel.

47. A method according to claim 46, further comprising using metering
structure to meter the amount of chlorine dioxide generating solution entering the
10 reaction vessel from the chlorine dioxide generating solution tank.

48. A method according to claim 46, further comprising using a chlorine
dioxide sensor in the vessel to measure and the amount of chlorine dioxide
present in the vessel and a controller for controlling the metering structure.
15

49. A method according to claim 41, wherein the air stream and flow of
activated solution through the column are counter current.

50. A method according to claim 41, wherein the method is a gas
20 scrubber, air washer, evaporative cooler, or humidifier.

51. A method of providing a liquid stream of chlorine dioxide comprising:
exposing a chlorine dioxide generating solution to UV light to form an
activated solution containing chlorine dioxide in a reaction vessel;
25 agitating said activated solution using a source of ultrasonic vibrations to
drive chlorine dioxide from said activated solution;
flowing an air stream through said vessel to form an air stream containing
chlorine dioxide;
transferring the air stream containing chlorine dioxide to a column in
30 communication with said reaction vessel; and
supplying a solvent into said column such that it contacts the air stream
containing chlorine dioxide to form a solvent containing chlorine dioxide.

52. A method according to claim 51, further comprising flowing the air stream and solvent through a packing material present in said column.

5 53. A method according to claim 52, wherein the packing material comprises one or more materials selected from the group consisting of NuPac, beads, saddles, cubes, pads, or irregular shaped pieces of plastic, ceramic, metal, or glass.

10 54. A method according to claim 51, further comprising using a mist eliminator disposed in the air stream path to reduce mist from entering the column.

15 55. A method according to claim 51, further comprising transferring chlorine dioxide generating solution from a chlorine dioxide generating solution tank into said reaction vessel and transferring chlorine dioxide generating solution from said vessel to said chlorine dioxide solution generating tank.

20 56. A method according to claim 51, wherein the flow of solvent and air stream containing chlorine dioxide are counter current in said column.

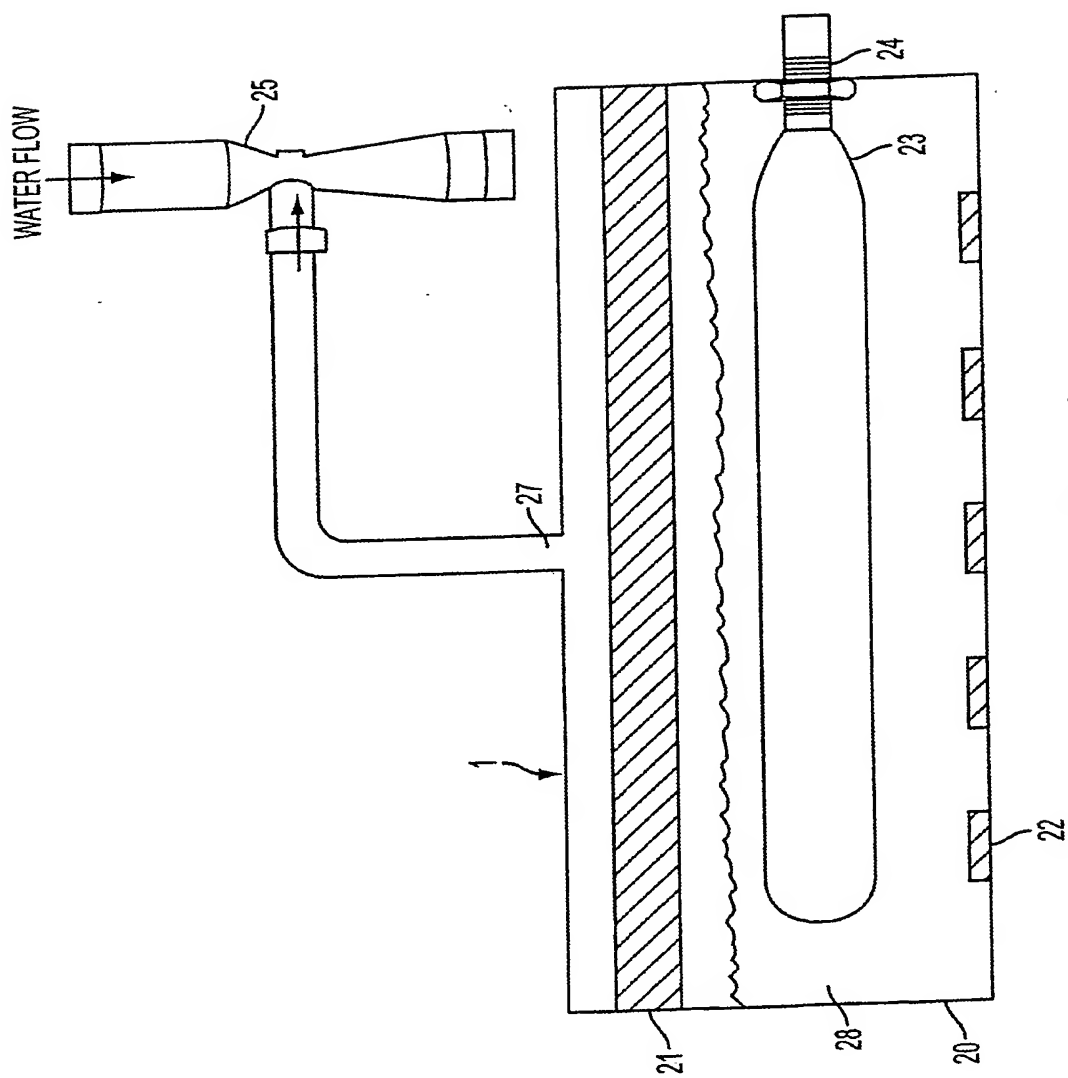


FIG. 1

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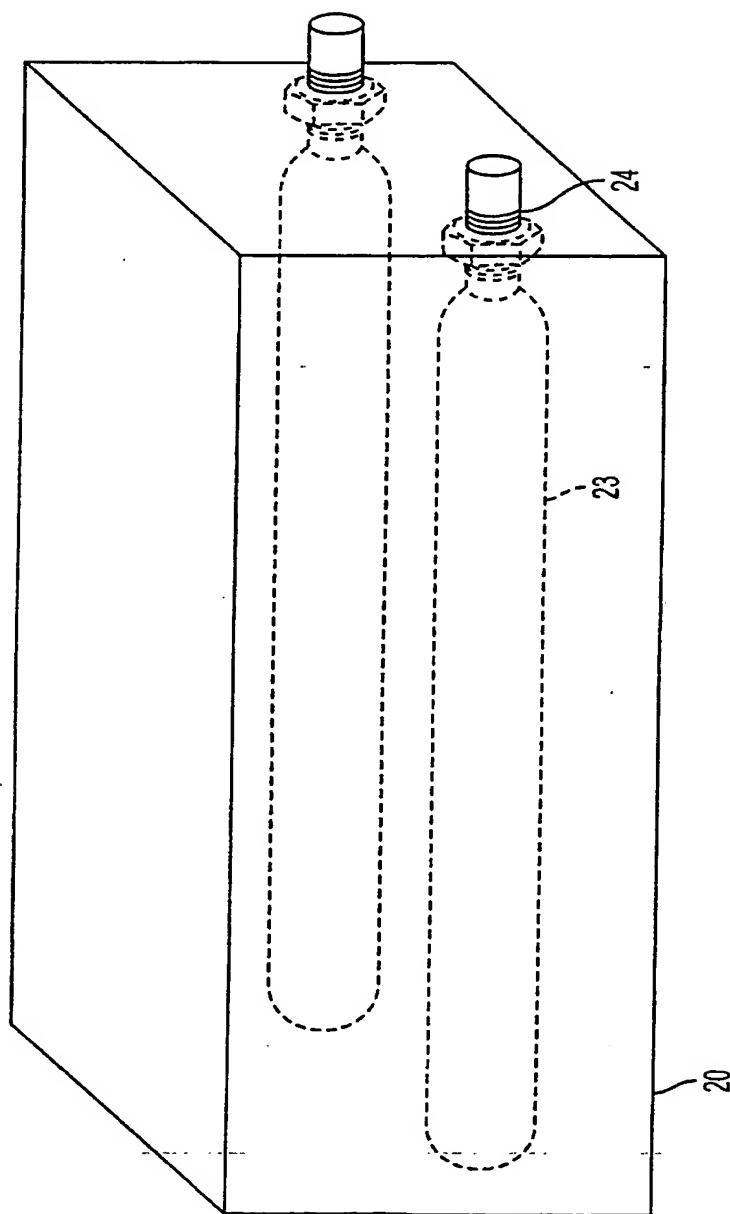


FIG. 2

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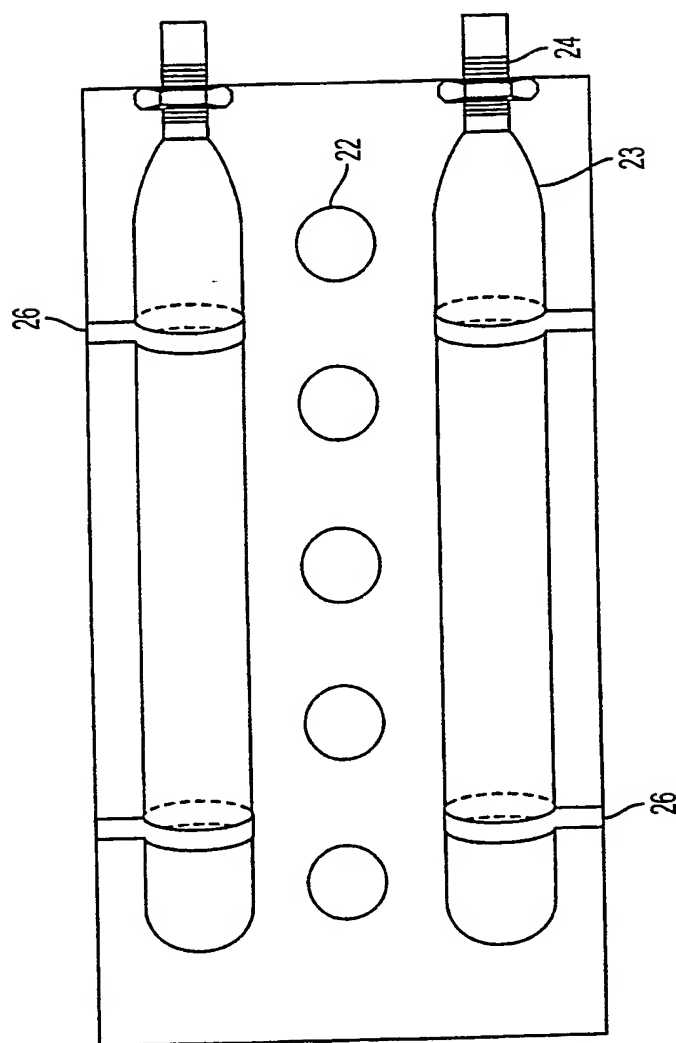


FIG. 3

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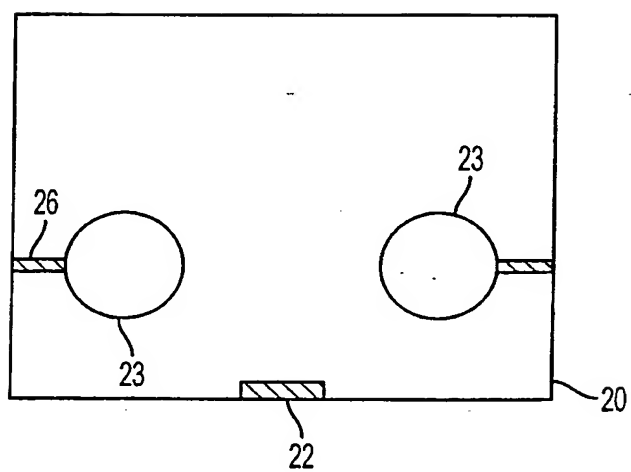


FIG. 4

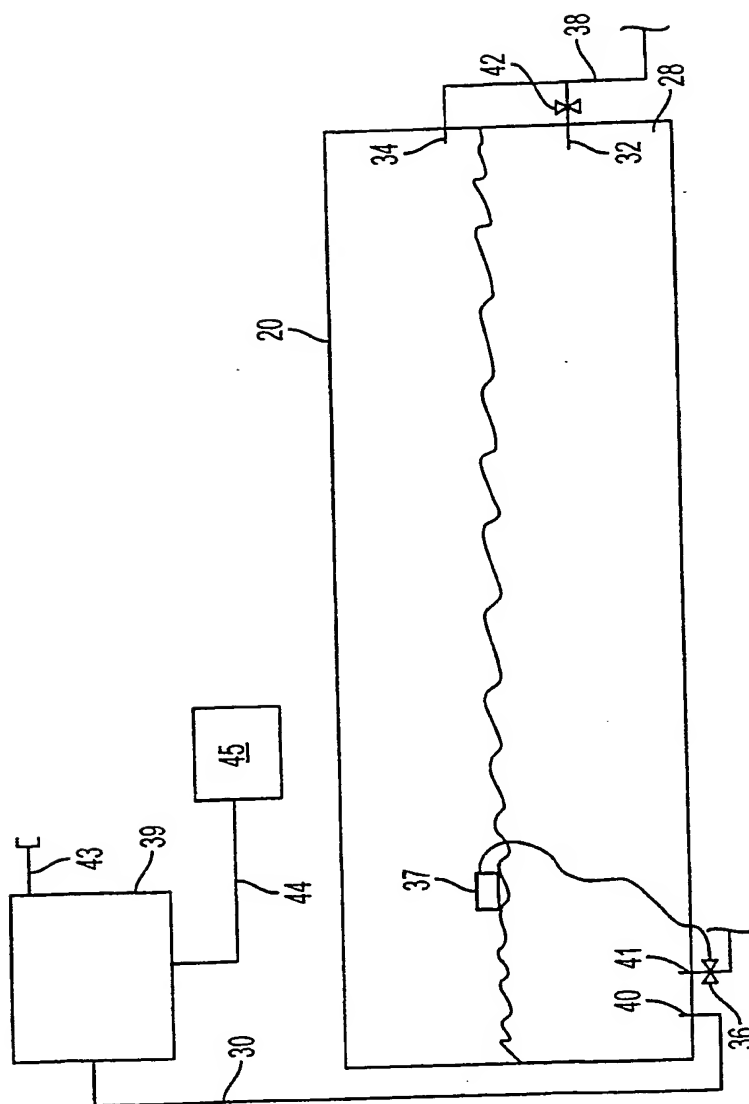


FIG. 5

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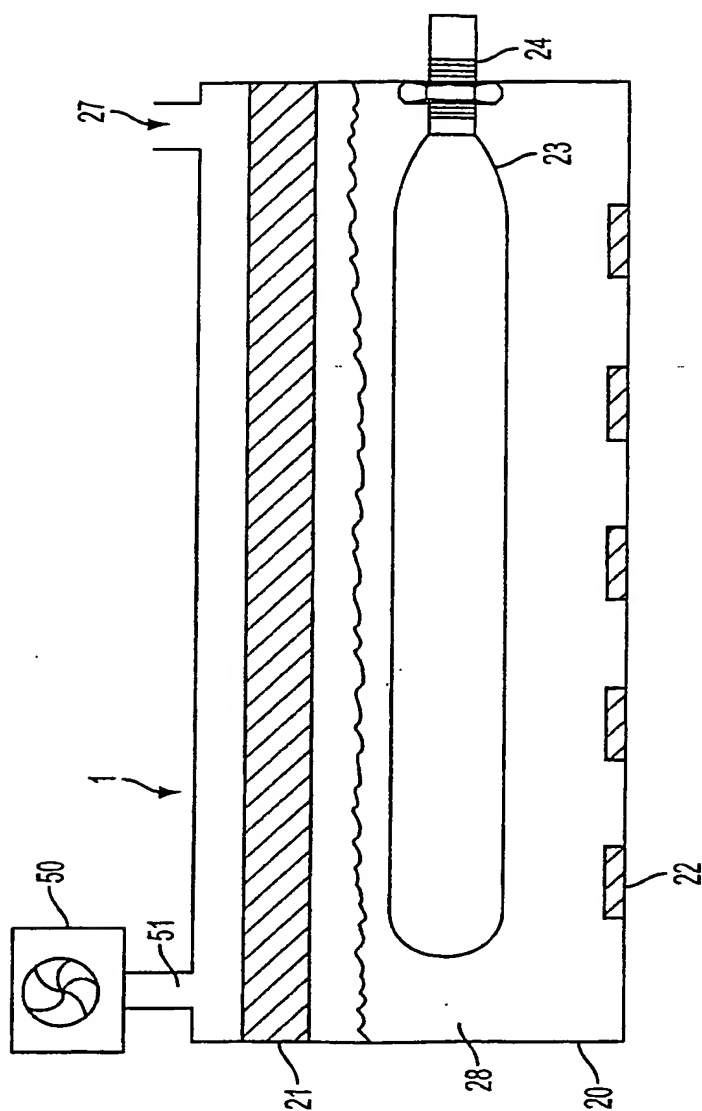


FIG. 6

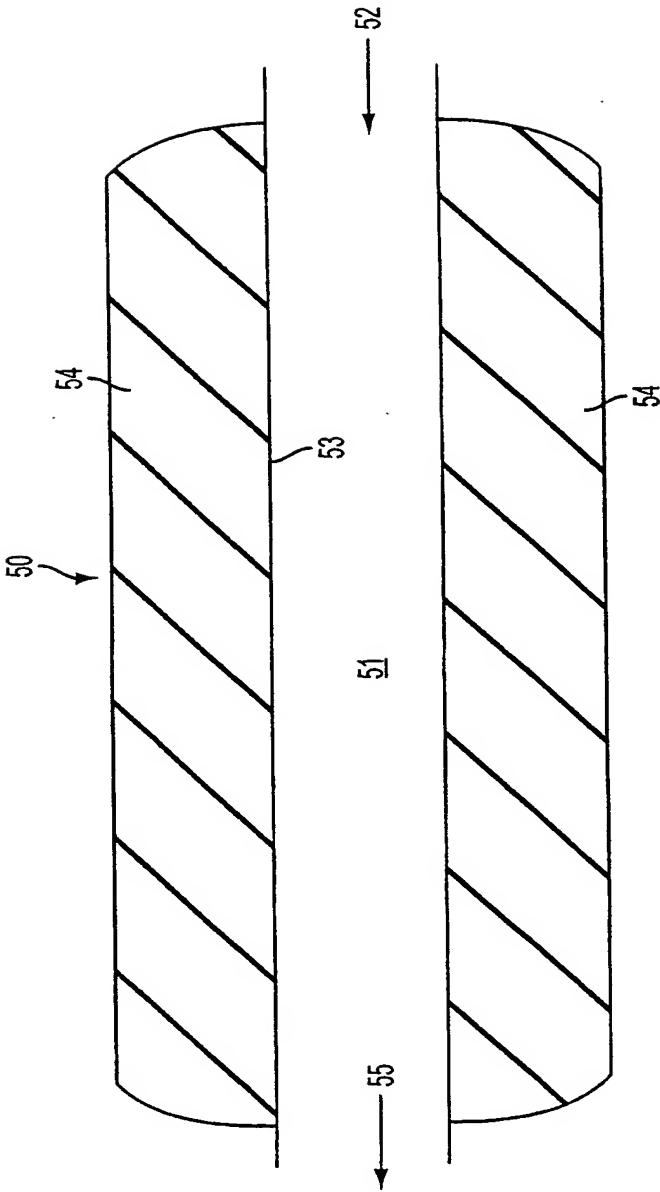


FIG. 7

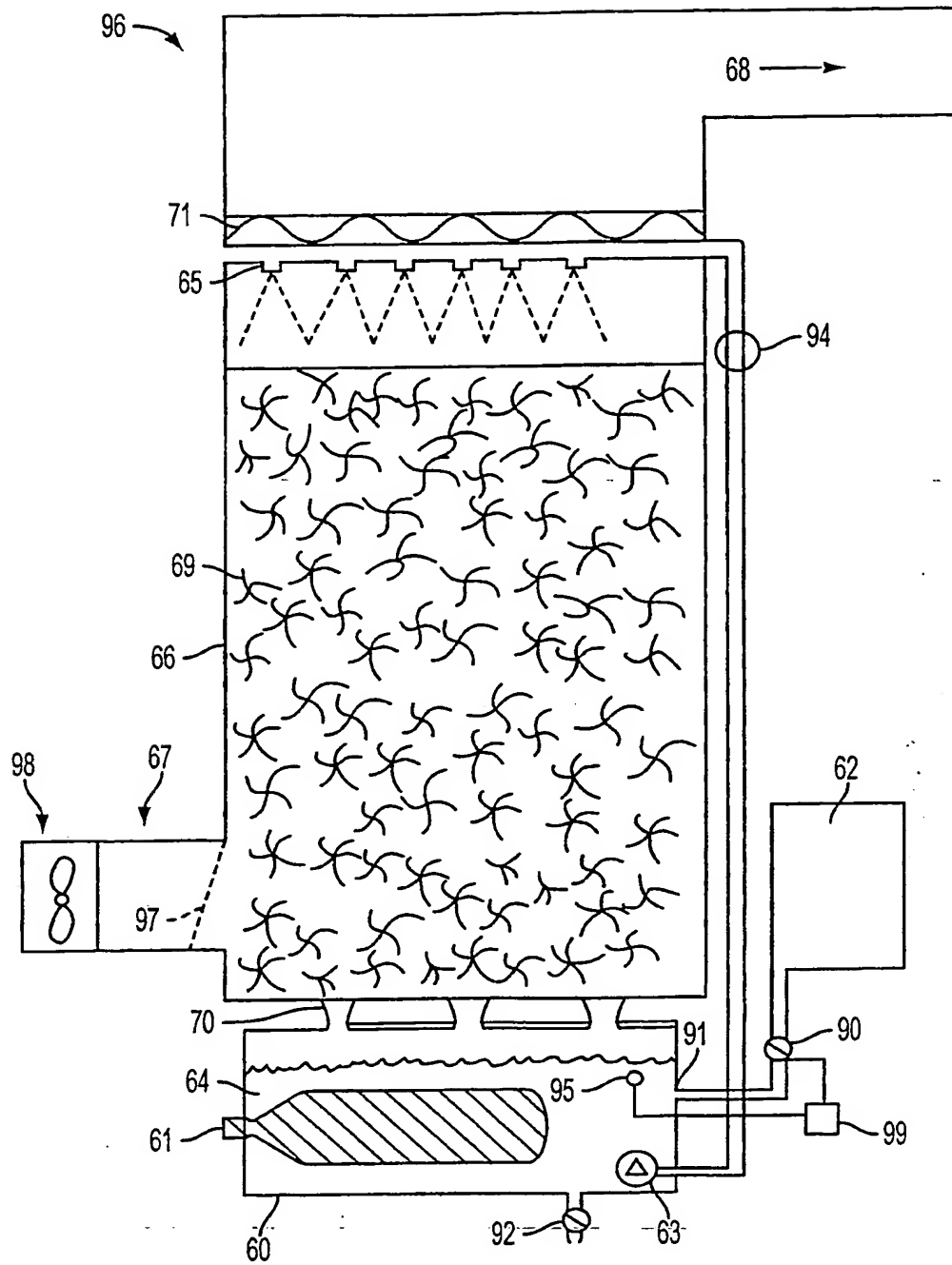


FIG. 8

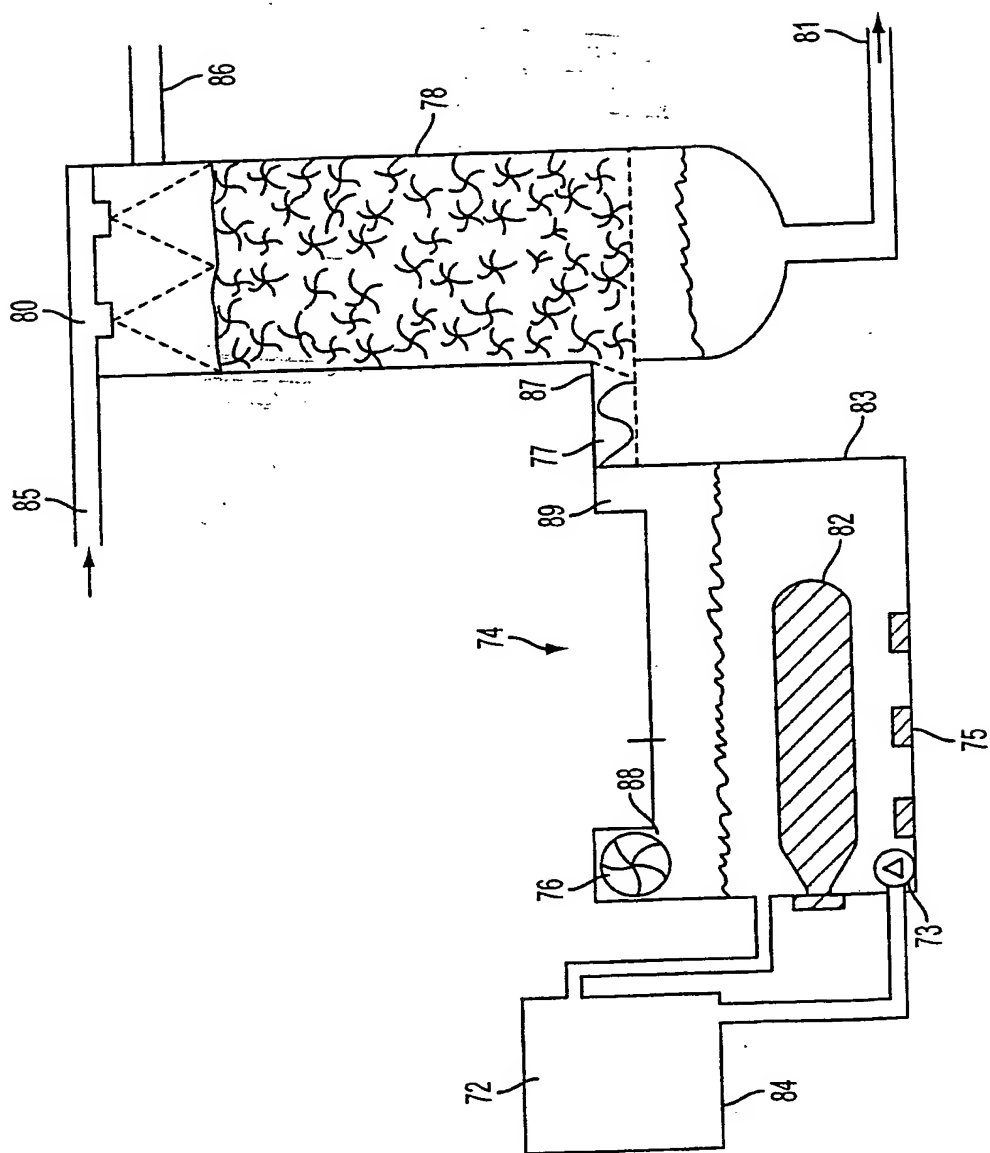


FIG. 9